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PAPER

Tm(III) complexes undergoing slow relaxation of magnetization: exchange coupling and aging effects†

A. Amjad,^a A. Figuerola^b and L. Sorace^{*a}

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Introduction

Magnetic relaxation phenomena in complexes qualifies that the system undergoes a magnetic field perturbation followed by the establishment of a new equilibrium state.^{1,2} If this is achieved by overcoming a magnetic anisotropy barrier between the two states, the relaxation time can be lengthened by increasing the height of the barrier.³ In this respect lanthanide based complexes^{4,5} are the leading contending complexes in showcasing slow relaxation of magnetization, with anisotropy barriers larger than 1000 K being recently reported.⁶ These high energy barriers are a consequence of the large single-ion magnetic anisotropy of these systems, due to the combined action of the strong spin-orbit coupling of 4f systems and of the strong axial symmetry of the obtained complexes.^{7,8} These features have ignited the synthesis, characterization and analysis of magnetic properties of single-ion magnets, SIMs,^{3,9–13} to exploit their expediency in applied sciences¹⁴ such as molecular spintronics^{15–18} and ultrahigh density magnetic memory devices.¹⁹ Lanthanide based molecular complexes have also been proposed as potential qubits for molecular quantum computing,^{20,21} thanks to their long decoherence time at low temperature,^{22,23} as well as in the understanding of the basic

The present study focuses on the dynamic magnetic behaviour of exchange coupled 3d–4f complexes containing the scarcely investigated non-Kramers Tm³⁺ center, the 3d metal ions being either the low-spin Fe³⁺ (**1**) or the diamagnetic Co³⁺ (**2**) ion. Both complexes display field-dependent slow relaxation of magnetization. The field and temperature dependences of the relaxation rate provided indication of relevant contributions from quantum tunnelling, direct and Orbach and Raman processes, with only minor effects from exchange coupling interactions. Furthermore, the aged sample of **2** exhibited an additional relaxation process, possibly due to solvent loss, highlighting the importance of a careful consideration of this factor when analysing the magnetization dynamics in solvated systems.

quantum phenomenon²⁴ like Quantum Tunnelling of Magnetization (QTM),²⁵ and as building blocks of molecular based refrigerants based on the magnetocaloric effect.²⁶

For a complex to behave as a pure SIM or SMM, the observation of slow relaxation of magnetization in zero field as opposed to field induced relaxation of magnetization is crucial,^{12,27,28} and this requires an accurate knowledge of the various mechanisms involved in the relaxation of magnetization (spin–lattice relaxation) which are the temperature dependent Direct process (with rate τ_{Dir}^{-1} (ref. 29)) and the two-phonon Orbach (with rate τ_{Orb}^{-1} (ref. 30)) and Raman processes (with rate τ_{Ram}^{-1}).^{31,32} Furthermore, the temperature independent process as Quantum Tunnelling of Magnetization (QTM, with rate τ_{QTM}^{-1} (ref. 33)) may also contribute. The global relaxation rate of magnetization of lanthanide based systems usually involves a combination of two or more of the aforementioned processes, with the most general behaviour portrayed in eqn (1):

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{\Delta}{k_B T}\right) + C T^n + A T H^m + a \left[\frac{(1 + b^2 H^2)}{(1 + c^2 H^2)} \right] \quad (1)$$

where in the first term Δ is the magnetic anisotropy barrier,³⁰ in the second term $n = 9–11$ for lanthanide based complexes, in the third term H is the external magnetic field and $m = 2$ or 4 depending on spin parity. Finally, the last term is the so-called Bruns–Van Vleck term that arises from the presence of local magnetic fields associated with spin–spin interactions, which might be important for the relaxation in relatively concentrated systems.³³ In this term, which can be related to the QTM in SMMs,^{27,30} a represents the zero field relaxation rate, c takes into account the ability of the external field to suppress

^aINSTM Research unit & Dipartimento di Chimica “U. Schiff”, Università degli Studi di Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino, FI, Italy.

E-mail: lorenzo.sorace@unifi.it

^bDepartament de Química Inorgànica i Orgànica, Secció de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1–11, E-08028 Barcelona, Spain

†Electronic supplementary information (ESI) available: Packing diagrams of complexes, powder X-ray diffraction patterns, dc magnetic characterization and additional ac susceptibility data. See DOI: 10.1039/c6dt04691f

this mechanism, while b , strongly dependent on the concentration of the spin centers, takes into account the field effects on the relaxation of interacting spins.^{33,34}

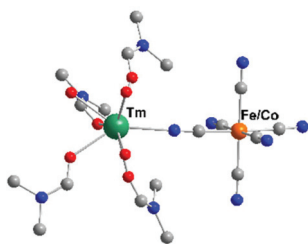
Following the complexity of the resultant relaxation rate behaviour, numerous reports are being devoted both to improving the slow dynamics feature of lanthanide complexes and the appropriate identification of the processes responsible for slow relaxation of magnetization.^{35–39}

An interesting approach to achieve slow dynamics and high energy barriers is the synthesis of 3d–4f compounds,^{9,40–42} where the 3d metal can be either paramagnetic or diamagnetic.^{43,44} In particular, when the 3d metal ion is paramagnetic, the exchange-coupling interaction is often able to reduce the quantum tunnelling of the magnetization, resulting in longer relaxation times.^{45–48} In this respect we thought it would be useful to evidence the effect of the exchange coupling by comparing the dynamic magnetic behaviour of isostructural systems where the 3d metal ion is either paramagnetic or diamagnetic. In detail, we focused on a family of complexes for which this strategy has already been successfully applied by two of us to the analysis of static magnetic behaviour.^{49,50} Since only scattered reports of magnetic properties of Tm^{3+} based compounds are available^{51,52} and until very recently no evidence of slow relaxation of magnetization existed in the literature for such complexes,⁵³ we decided to analyse the dynamic magnetic behaviour of $\text{Tm}(\text{dmf})_4(\text{H}_2\text{O})_3(\mu\text{-CN})\text{-X}(\text{CN})_5\cdot 1.25\text{H}_2\text{O}$ compounds. Here, $\text{X} = \text{Fe}^{3+}$ (**1**), Co^{3+} (**2**) with both 3d ions being in their low spin state due to the hexacyanide coordination.⁴⁹ The basic structural unit of this molecule is shown in Scheme 1: the coordination polyhedron around the Tm^{3+} ion showcases a bicapped trigonal prism geometry and the X^{3+} ion sits in a distorted octahedron.⁵⁰ The unit cell comprised of four discrete heterodinuclear molecules is shown in Fig. S1.†

The combined magnetometric and powder EPR studies showed that at low temperature the behaviour of **1** could be modelled using the following spin Hamiltonian acting between the two anisotropic pseudo $S = 1/2$ of the constituent paramagnetic ions:

$$\hat{H}_{\text{EPR}} = J_{\text{iso}}\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_1 \cdot \mathbf{D} \cdot \mathbf{S}_2 + \sum_{i=1,2} \beta \mathbf{H} \cdot \mathbf{g}_i \cdot \mathbf{S}_i \quad (2)$$

The assumption of Tm^{3+} behaving as a pseudo doublet was reinforced by the observation of a single EPR transition in **2**,



Scheme 1 View of the molecular structure of **1** and **2**. Blue balls: nitrogen atoms; red balls: oxygen atoms; grey balls: carbon atoms.

which could be modelled assuming $S_{\text{eff}} = 1/2$, $g_{\text{eff}}^z = 14$, i.e. a potentially relevant Ising-type anisotropy. By keeping the number of parameters to a minimum the experimental results on the coupled system could be semi-quantitatively modelled assuming $g_{\text{Fe}} = (2.0, 0.7, 2.5)$, $g_{\text{Tm}} = (0.1, 0.1, 15)$, $J_{\text{iso}} < 0 \text{ cm}^{-1}$ (i.e. ferromagnetic interaction), $D_{xx} = D_{yy}$ and $D_{zz} \geq 8 \text{ cm}^{-1}$. As a whole they demonstrated the existence of a non-negligible anisotropic ferromagnetic exchange coupling interaction between $\text{Fe}(\text{III})$ and $\text{Tm}(\text{III})$.^{50,54}

Inspired by these preliminary results, suggesting that these systems might behave as SIMs, herein we present extensive exploration of their magnetization dynamics over a wide range of frequency, direct current (dc) magnetic field, temperature and aging time. The study revealed that both complexes show slow relaxation of magnetization, but only in the presence of an external magnetic field. The field and temperature dependences of the relaxation rate provided indication of relevant contributions from quantum tunnelling, direct and Raman processes, with only minor effects from exchange coupling interactions. Furthermore, the aged sample of **2** exhibited an additional relaxation process, possibly due to solvent loss, a factor only seldom considered in the analysis of the magnetization dynamics of solvated systems.^{55,56}

Experimental section

The samples were synthesized as previously reported in the literature.⁴⁹ The alternating current (ac) magnetic susceptibility investigations were performed on polycrystalline samples pressed in a 5 mm pellet. The measurements were executed by using a Quantum Design PPMS in ac mode, with a 5 Oe oscillating magnetic field, for the 10 Hz to 10 kHz frequency range. The slower dynamics was probed using a Quantum Design MPMS SQUID magnetometer (0.1 Hz to 1 kHz). The same SQUID was employed to explore the dc magnetic susceptibility measurements in a 1 kOe dc magnetic field and the isothermal magnetization at different temperatures (1.9, 2.5, 4.5 K). The polycrystalline samples used for magnetic characterization were previously evaluated by X-ray powder diffraction technique using a Bruker D8 advance powder diffractometer equipped with a Cu source (K_{α} , $\lambda = 1.54 \text{ \AA}$) (see Fig. S2†).

Results and discussion

Preliminary dc characterization was performed to ensure that the magnetic behaviour of the two complexes was consistent with that reported in the literature. This was indeed the case, as reported in Fig. S3.†^{43,51}

Ac susceptibility

Ac susceptibility measurements were carried out to explore the slow magnetic relaxation dynamics of **1** and **2**. No imaginary component of the susceptibility was observed for both samples between 10 Hz and 10 kHz even at the lowest investi-

gated temperature (2 K), with no applied field. However, a field induced, frequency dependent maximum was observed in χ'' for both complexes at 2 K, indicating that the complexes undergo field-induced slow relaxation of magnetization (Fig. 1 and 2). The low temperature (2 K) relaxation dynamics of **1** as a function of external dc magnetic field is shown in Fig. 1a-inset (additional data are reported in Fig. S4†). It is quite clear that only a small field ($H > 250$ Oe) is required to trigger the slowdown of magnetization dynamics in **1**. The observed behaviour has been reproduced using the generalized Debye model³⁰ (solid lines in Fig. 1a-inset), which allowed us to extract the corresponding relaxation time as a function of magnetic field (Fig. 1a, main panel). The relaxation time passes through a maximum around 1 kOe, and then rapidly decreases at higher field, suggesting a competition between quantum tunneling and direct relaxation processes. Accordingly, these data were analytically reproduced using eqn (1) with the appropriate terms.⁵⁷ The best fit parameters, providing the solid line in Fig. 1a, main panel, are reported in Table 1 and clearly point to the persistence of non-negligible QTM even at a relatively high field. This is a somehow unexpected occurrence, since in lanthanide based complexes, QTM is usually quenched in the presence of moderate dc magnetic fields.^{43,58} Furthermore, the direct process shows a H^2 dependence as

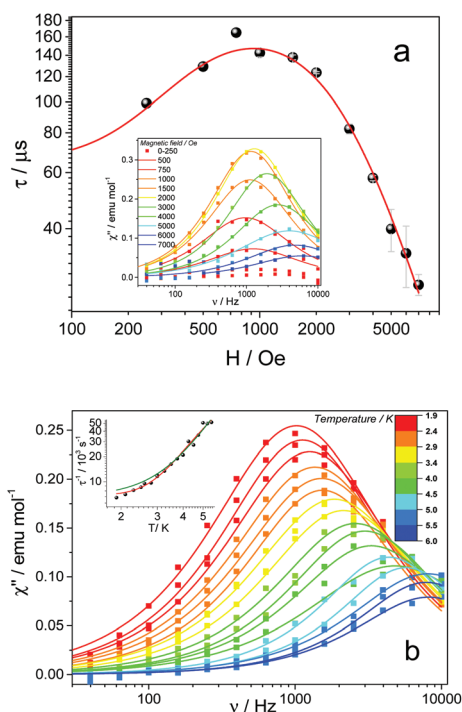


Fig. 1 (a) Plot of relaxation time of **1** at 2 K as a function of applied magnetic field, (inset) field response of the out-of-phase χ'' susceptibility signal of **1** measured at 2 K, the lines are fits using the Debye expression. (b) Temperature behaviour of χ'' of **1** measured at 1 kOe (solid lines are the Debye fits), (inset) extracted relaxation times as a function of temperature at 1 kOe. The solid red line corresponds to the best fit obtained using the Orbach process as the leading temperature dependent one, green line to the Raman one.

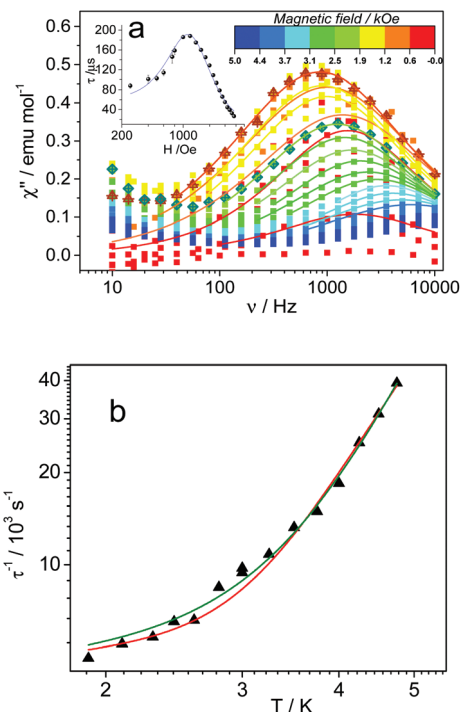


Fig. 2 (a) Magnetic field dependence of the out-of-phase χ'' susceptibility signal of **2** measured at 2 K and variable frequencies (lines are fits using the Debye expression): 1 kOe and 2 kOe data are highlighted with different symbols. In the inset the extracted relaxation times plotted against the magnetic field are shown. (b) Temperature dependence of the magnetic relaxation time of a freshly pressed pellet of **2**, measured in a field of 1 kOe. The solid red line corresponds to the best fit obtained using the Orbach process as the leading temperature dependent one, green line to the Raman one.

expected for a non-Kramers' ion; this is not obvious since **1** features an odd number of electrons. As the maximum in relaxation time is observed between 1 kOe and 2 kOe for **1**, these two extreme fields were chosen to conduct the study of the dynamics as a function of temperature. The maximum in the out-of-phase susceptibility is observable, within the range of available frequencies, up to 9 K (Fig. 1b-main panel and Fig. S5†). At the lower temperature ends, there is still a quite evident temperature dependence at both fields, indicating that the thermally independent QTM process is not dominating the relaxation. The corresponding relaxation times extracted at each magnetic field are shown in Fig. S6.† When reported in an Arrhenius plot, a deviation of relaxation time from a linear curve is clearly observed (Fig. 1b-inset), indicating that the relaxation mechanism is not of pure Orbach type but should consider all other terms of eqn (1).⁵⁹ It was further noted by the comparison of the temperature dependence of the relaxation rate measured at the two different fields that a strictly similar behaviour holds. The only difference is observed at $T < 3$ K, the 2 kOe data evidencing a faster relaxation, a signature of the relevance of the direct process, the rate of which increases with the magnetic field.

Table 1 Best fit parameters to field and temperature dependence of the magnetic relaxation rate in **1**^a

	Direct A/K s ⁻¹ Oe ⁻²	Quantum tunneling			Raman		Orbach	
		a/s ⁻¹	b/Oe ⁻²	c/Oe ⁻²	C/s ⁻¹ K ⁿ	n	Δ/K	τ ₀ ⁻¹ /s ⁻¹
2 K vs. <i>H</i>	(3.3 ± 0.4) × 10 ⁻⁴	15 956 ± 1066	(3.1 ± 0.8) × 10 ⁻³	(5 ± 1) × 10 ⁻³	—	—	—	—
1 kOe vs. <i>T</i>	(3.3 ± 0.4) × 10 ⁻⁴	15 956 ± 1066	(3.1 ± 0.8) × 10 ⁻³	(5 ± 1) × 10 ⁻³	87 ± 40	3.7 ± 0.3	16 ± 1	(9 ± 2) × 10 ⁵
2 kOe vs. <i>T</i>	(3.3 ± 0.4) × 10 ⁻⁴	15 956 ± 1066	(3.1 ± 0.8) × 10 ⁻³	(5 ± 1) × 10 ⁻³	20 ± 2	4.42 ± 0.06	21.0 ± 0.6	(1.7 ± 0.2) × 10 ⁶

^a *A*, *a*, *b* and *c* were determined by field dependent analysis and kept fixed for temperature dependent ones. Orbach and Raman processes were considered as mutually exclusive to reduce over parametrization.

These qualitative considerations were indeed confirmed by fitting the temperature dependence of the relaxation rate using eqn (1) (Fig. 1b and S6†), keeping the parameters derived by the field dependent data set fixed. To avoid over parametrization we further restricted our fit to two different options: either considering the two-phonon Orbach or the Raman one as the leading temperature-dependent relaxation term. The two approaches provided fits of similar quality at both fields, making it impossible to discriminate between the two possible processes. The best fit parameters obtained by this procedure are reported in Table 1.

A similar study was performed on **2**. Fig. 2a-main panel and Fig. S7† show the magnetization dynamics of **2** for magnetic fields varying from 0 to 5 kOe, and the inset of Fig. 2a shows the extracted relaxation times and their best fit achieved with parameters reported in Table 2. We note that the accuracy of the fit is reduced for points below 800 Oe: this might be attributed to noisier raw data, hampering an accurate derivation of the relaxation time. At any rate, the field dependence clearly evidence that, as observed for complex **1**, QTM and direct processes play a crucial role in the reversal of magnetization of **2**.

Since a maximum in relaxation time is observed at 1 kOe this field was chosen for temperature dependent ac susceptibility experiments. This choice was further induced by the analysis of the width of the distribution parameter on field variation, which achieves a maximum at 1 kOe (Fig. S7†-right) and a minimum at 2 kOe, thus making the latter another interesting field value to explore the dynamics.

The temperature dependent study at 1 and 2 kOe dc magnetic field evidence maxima in χ'' at about 1 kHz in **2**, moving out and fading away from the experimental range at a higher temperature (Fig. S8 and S9†). The peaks observed in the ima-

ginary component were reproduced with the Debye model to extract the corresponding relaxation time at 1 kOe (Fig. 2b) as a function of temperature. The absence of a linear behaviour over the whole temperature range in the Arrhenius plot (Fig. S10†) suggests that also in this system the temperature-dependent relaxation is not dominated by a simple Orbach process. Accordingly, we performed quantitative analysis of the data by following the same strategy as for **1**. This approach resulted in fits of comparable quality assuming Orbach or Raman terms as the dominant temperature dependent term (Table 2). The relaxation times obtained from the 2 kOe susceptibility curves along with the 1 kOe relaxation times for comparison purposes are shown in Fig. S10.† It is worth noting that, if one assumes this as the leading term, the exponent *n* of the Raman process observed for both complexes is, for both complexes quite smaller (3.5–5.5) than the value expected on the basis of an approximate theoretical model (*n* = 9–11).²⁹ However, a smaller *n* value is now almost routinely reported for molecular based complexes and attributed to both acoustic (lattice) and optical (molecular) vibrations taking part in the relaxation process.^{32,60} On the other hand, consideration of the two phonon Orbach process would require electronic/magnetic states that can be thermally accessible. This could only be obtained either by *ab initio* calculations or advanced spectroscopic characterization which are beyond the scope of this manuscript.^{28,38,61}

Comparison of dynamic magnetic properties of **1** and **2**

Up to now, only a single example of Tm³⁺ based complexes behaving as SIM in zero field has been reported in the literature, despite the fact that the prolate shape of the charge distribution of its *m_J* = ±6 should be favoured by equatorial type ligands.⁵³ This is usually attributed to the non-Kramers nature

Table 2 Best fit parameters to field and temperature dependence of the magnetic relaxation rate in a freshly pressed pellet of **2**^a

	Direct A/K ⁻¹ s ⁻¹ Oe ⁻²	Quantum tunneling			Raman		Orbach	
		a/s ⁻¹	b/Oe ⁻²	c/Oe ⁻²	C/s ⁻¹ K ⁻ⁿ	n	Δ/K	τ ₀ ⁻¹ /s ⁻¹
2 K vs. <i>H</i>	(9.3 ± 0.5) × 10 ⁻⁴	17 150 ± 4500	0	(2.0 ± 0.3) × 10 ⁻³	—	—	—	—
1 kOe vs. <i>T</i>	(9.3 ± 0.5) × 10 ⁻⁴	17 150 ± 4500	0	(2.0 ± 0.3) × 10 ⁻³	6.8 ± 1.5	5.4 ± 0.2	22 ± 1	(3.1 ± 0.7) × 10 ⁶
2 kOe vs. <i>T</i>	(10 ± 10) × 10 ⁻⁴	34 300 ± 4500	0	(2.0 ± 0.3) × 10 ⁻³	3.4 ± 1.9	5.4 ± 0.3	24.8 ± 0.9	(2.9 ± 0.5) × 10 ⁶

^a *A*, *b* and *c* were determined by field dependent analysis and kept fixed for temperature dependent ones. Orbach and Raman processes were considered as mutually exclusive to reduce over parametrization.

of the ion, coupled to the difficulty in obtaining a purely uniaxial symmetry, which leads to efficient mixing of m_j states and faster relaxation promoted by QTM.⁶² Even field induced slow magnetic relaxation has been scarcely reported in the past for Tm^{3+} complexes.^{51,52a,63} In addition to increase this small number of slow relaxing Tm^{3+} complexes our study was aimed at investigating the effects on the dynamics properties when the transition metal coordinated ion is either paramagnetic and exchange-coupled ($\text{Tm}^{3+}\text{-Fe}^{3+}$), or diamagnetic ($\text{Tm}^{3+}\text{-Co}^{3+}$). The comparison between the observed spin dynamics of complexes **1** and **2** in fixed temperature, variable field and *vice versa* conditions, is shown in Fig. 3(a and b).

As discussed above spin dynamics in both complexes followed a temperature dependent behaviour typical of slow relaxation of magnetization triggered by multiple mechanisms (Tables 1 and 2). While the effect of temperature on τ^{-1} is almost identical in the two cases, a more pronounced difference in the relaxation rate is evident in the field dependence at 2 K. Indeed, the longest relaxation time, observed for both complexes in the 1–2 kOe range, is almost 30% slower for the Co^{3+} derivative than for Fe^{3+} one. This is in contrast with the common view that the presence of an exchange-coupled centre should induce a bias field on the adjacent spin, resulting in a less effective QTM process.⁶⁴ Apparently, in this case, this mechanism is only active at relatively high fields, where the

Fe^{3+} derivative relaxes slower than the Co^{3+} one. Fig. 3 shows quite similar responses to the magnetic field and temperature for both complexes, confirming that the exchange interaction between the Tm^{3+} and the Fe^{3+} ion is not crucial in driving the relaxation. In this respect, it appears that the Raman process should be considered as more likely than the Orbach one to be the dominant temperature dependent term in the relaxation. One would indeed expect the latter to be largely different in the two cases, following the non-negligible exchange interaction characterizing **1** as compared to **2**. This is not the case for the Raman process.

Evolution of magnetic dynamics of [$\text{Tm}^{3+}\text{-Co}^{3+}$] with ageing

While studying the magnetization dynamics of complex **2** we noticed the progressive emergence of a new, additional maximum in the out-of-phase susceptibility signal on ageing of the sample. This was missing in the freshly pressed pellet, while a three-month old pellet showed a weak peak at low frequencies (Fig. S11†). This prompted us to monitor the dynamics of **2** on an aged sample (six months), since we thought this aspect could be of interest for the general community of molecular magnetism. The signature of a second well pronounced slow relaxation (hereafter SR) process was found to overlap with a process closely resembling the one of the freshly pressed sample (see above), which was faster (hereafter termed a fast relaxation process, FR). An extensive set of ac measurements as a function of temperature and field revealed that at low temperatures only the FR process is visible, followed by a coexistence of both the processes at 4 K, eventually leading to an almost complete suppression of the FR one and the dominance of the SR process, approximately above 10 K (Fig. S12–S16†). The extrapolated field dependent relaxation times of both processes at variable temperature are reported in Fig. 4(a and b).

For the FR process (Fig. 4a), at 2 K the relaxation rate is observed to increase at weak fields, followed by a plateau above 1 kOe. The observed increase in the relaxation rate is consistent with the results reported above for the freshly prepared sample. Higher temperatures led to gradual decrease in τ , until, above 1 kOe and 3 K, the relaxation rate becomes almost temperature independent up to 8 K. The SR process could be analysed at higher fields (1–10 kOe, Fig. 4b), the corresponding maximum in χ'' being clearly observable only above 4 K. The field dependence of this process at 8 K is evidence of a smooth increase in the rate up to 4 kOe followed by a linear decrease at higher fields. This clearly indicates that also for the SR process the direct and QTM mechanisms are active and dominating in different field regions, with an intermediate field region (2.5–3.8 kOe) where they govern the relaxation equally. The fact that slow relaxation of magnetization is governed by multiple mechanisms is quite expected, not only in lanthanide-based complexes but in other magnetic materials as well.^{43,53,58,65}

The analysis of relaxation time under different conditions summarized in Fig. 4, also corroborated that the SR process is essentially evident at high temperature and high field. This

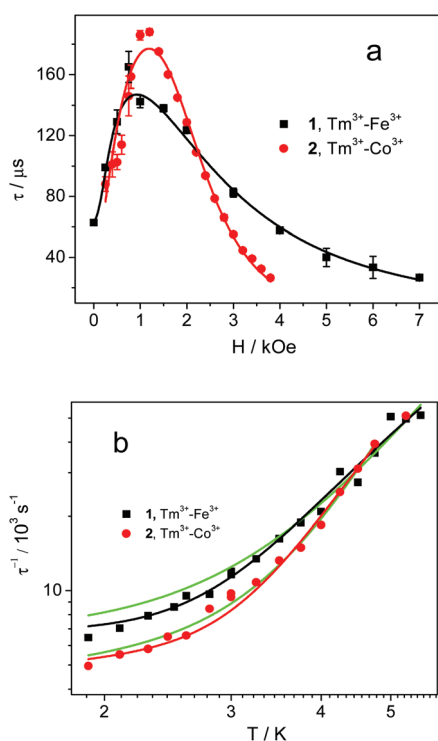


Fig. 3 (a) Field dependence of the magnetization relaxation time for **1** and **2** measured at 2 K: best fit lines obtained using parameters reported in Tables 1 and 2. (b) Temperature dependence of the relaxation rate for **1** and **2** measured in an applied static field of 1 kOe. The solid black and red line correspond to the best fit obtained using the Orbach process as the leading temperature dependent one, green line to the Raman one.

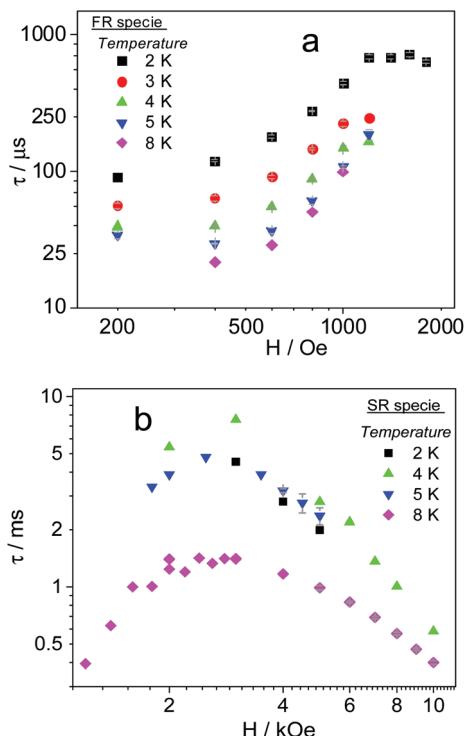


Fig. 4 Relaxation time as a function of static magnetic field for complex 2 (6-month old pellet) for fast (a) and slow (b) relaxing species. Data points are missing at certain fields and temperature due to the merging of the peaks pertaining to the two different processes.

was exploited and confirmed by conducting temperature dependent ac susceptometry scans at 1, 2, 5 and 10 kOe on the aged sample (Fig. S17–S20†). It is quite clear that only the FR process is active at 1 kOe, while the SR process dominates at higher fields, with a coexistence region around 2 kOe, where peaks of the two processes overlap. The relaxation times obtained by Debye fitting of these data are shown in Fig. S21† for the FR process and in Fig. 5 for the SR one. The latter data

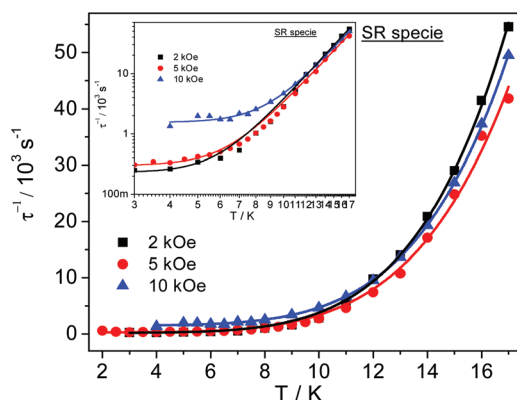


Fig. 5 Temperature dependence of the relaxation rate of complex 2 (6-month old pellet) for the SR species at different magnetic fields and best fit curves obtained using parameters reported in Table S1.† The inset shows the corresponding Arrhenius plots.

were fitted to eqn (1), providing the best fit parameters reported in Table S1† (corresponding curves are shown as solid lines in Fig. 5). It is quite clear that the Raman process is essentially field independent as should be the case, with the n value in close proximity to that observed for the fresh pellet. The anomaly, already evident by a qualitative analysis of the experimental data, is that QTM increases on increasing dc magnetic field, as highlighted in the Arrhenius plot (inset of Fig. 5). A possible explanation for such anomalous behaviour stems from the energy landscape boasting a ground singlet and an excited (pseudo)doublet. In the presence of a magnetic field, and with an increase in magnitude, the (pseudo)doublet split and the energy difference between the lower doublet and the ground singlet decreases. This in turn leads to faster relaxation times *via* quantum tunnelling of magnetization. This is, however, a best-case consequence, as structural and energy pattern details of the aged samples are not available to further corroborate this point.

Additional information acquired from the behaviour of aged samples at variable field and temperature led to two important conclusions. First, the number of molecules undergoing each process is varying with field and temperature. The dominance of species relaxing through one process over the other is quite clear (Fig. S12–S20†), the FR being the dominant process at low field and low temperature (2 K, 1 kOe), while the SR dominates at higher fields and frequencies (5 K, 3 kOe and higher) with a smooth transition between the two regimes. Concurrent to this, one can note the shift of the peak of the FR process in the aged sample to slightly lower frequencies compared to the fresh sample. This insinuates that even if this process can be in principle attributed to the same specie responsible for that observed in the fresh sample, it is however slower for aged samples (Fig. S22†).

The set of results described in this section were challenged and put to test by a comparative study performed on a new freshly pressed pellet. The dynamics as a function of temperature and magnetic field showed a complete overlap with the previous data, with no additional peaks in χ'' (Fig. S23†). In conjunction, the time evolved emergence of the unique moieties in complex 1 was also investigated at several temperatures and fields *via* ac susceptibility measurements after a period of six months. Interestingly, no indication of a second relaxation process was observed (Fig. S24†).

Discussion on ageing

It is well known that both local molecular symmetry and intermolecular interactions play a crucial role in determining the low temperature magnetization dynamics in molecular complexes.⁶⁶ In the previous section it has been experimentally proven that two unique relaxation processes (FR, SR) coexist in the cobalt derivative because of the aging of the pellet under study. We tentatively attribute this behaviour to the formation of two different species, in a way similar to that first suggested for Mn_{12} polynuclear SMMs.^{67–69} In that case the observed behaviour was attributed to the fact that a certain percentage of the molecules possessed different molecular structures from

the majority ones, which led to different anisotropies. A similar behaviour has been later reported also in lanthanide based complexes.^{55,56,70,71} In the present case, the heterodinuclear structural units of **2** form a 3D network with water molecules from crystallization;⁴⁹ it can then be suggested that when the sample was pressed into a pellet this resulted in a partial loss of solvent. This hypothesis is confirmed by the powder X-ray diffractogram, showing that the aged sample is made up by a different crystalline phase (ESI, Fig. S1†). Elemental analysis, on the other hand, is consistent with the loss of both parts of lattice water molecules and of formamide ligands (see ESI Table S3†). On the other hand, the iron derivative turned out to be immune to aging effects and hosts only one species.

So far we pointed out that ageing of the sample led to emergence of a new species, characterized by the SR process; however, as anticipated in the earlier section, the spin dynamics of the FR species also evolved with time (Fig. S22†). This is illustrated in detail in Fig. 6(a and b), where a comparison of the FR dynamics for the new and six month old sample is reported. Under identical magnetic field and temperature conditions, the aged sample showed a slower relaxation rate, but the field and temperature dependencies are different for the two samples. For both samples τ is observed to be almost field-independent for the two samples until 400 Oe, then increases with respect to the increasing field to reach the

respective, different, maxima (see also Table S2†). We note that for the aged sample higher field points are lacking, since in this region this contribution is masked by that of SR species. On the other hand, variable temperature data at a fixed field of 1 kOe, show the two samples following a similar temperature dependence up to 3 K, followed by a more marked decrease for the fresh sample and an almost temperature independent one for the aged one (see also Table S2†).

Obviously, a similar study could not be performed for SR species, since this appears only in the aged sample. However, since SR species relaxation is visible at high temperature and field, it was deemed thorough to probe the field dependence of the ac susceptibility of the fresh sample at a high temperature. The resulting in- and out-of-phase components as a function of frequency performed at 5 K on the new sample, along with the behaviour of the alpha parameter are shown in Fig. S25.† A clearly defined single peak is observed at exactly the frequency expected from the earlier data. The corresponding field dependence of τ at 2 K and 5 K is shown in Fig. S26.† This reaffirms the fact that only FR species exists in the new sample and SR species is due to aging and is a high field, high temperature process.

Conclusions

In this paper, we have demonstrated that two Tm^{3+} based complexes, either single-ion or exchange-coupled, undergo field-induced slow relaxation of magnetization. For both derivatives, the observed dependence of relaxation time τ on the field and temperature evidenced that multiple processes are at work. A stepwise fit procedure of both field and temperature dependent magnetic relaxation time clearly evidenced the contributions of the direct process and of quantum tunnelling of magnetization. As the leading temperature-dependent relaxation term the fit did not provide conclusive evidence of the relaxation occurring *via* a two-phonon Orbach process or a Raman one. However, a similar behaviour observed in the two complexes led us to favour the latter process which could be less affected by the exchange interaction active in **1**. As a whole, this study points out once more that the observation of field induced slow relaxation of the magnetization is not, by itself, an indication of single molecule magnet behaviour (*i.e.* an over barrier relaxation which can be tuned by chemical means).

The analysis of the dynamic properties of the two complexes further pointed out that on aging the Co^{3+} derivative evolves to produce an extremely complex behaviour, whereas the Fe^{3+} was found immune to such changes. The likely formation of two different species resulted, for the former derivative in two different relaxation processes observable as a function of field, temperature and age of the sample. In this respect, the present paper suggests that the spin dynamics of the lanthanide based complexes must be extensively scrutinized to isolate/identify the ageing effects in order to deepen

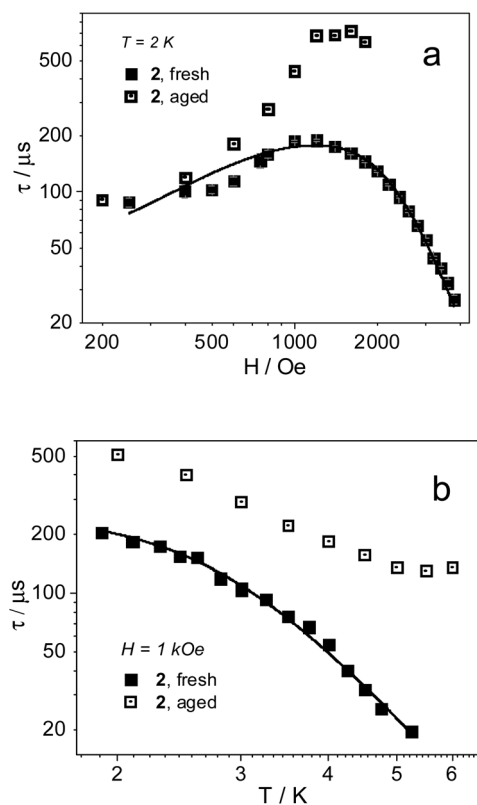


Fig. 6 Comparative behaviour of τ of FR species as a function of field (a) and temperature (b) for a fresh and aged pellet in complex **2**.

the understanding of the origin of reversal of magnetization under a vast range of experimental conditions.

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